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An Insight into the Barton Equation for Copolymer Glass Transition

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ABSTRACT: New expressions of the Barton equation for the copolymer glass transition temperature T_g are derived to make its potential characteristics clear. On a plot of T_g against the run number R instead of composition, (i) the arithmetic mean of the homopolymer T_g values, the T_g of the equimolar random copolymer, and the T_g of the corresponding alternating copolymer are on the same straight line and (ii) T_g values of two random copolymers having a given value of R, but different compositions, deviate equally from the line mentioned above. Applications of the new expressions to three different typical data in the literature are illustrated as demonstrations of potentials of the equations.

Introduction

As is well-known, the glass transition temperatures of copolymers deviate from linear relations such as the DiMarzio–Gibbs equation[1]

$$T_g = m_A T_{gA} + m_B T_{gB} \tag{1}$$

Here, T_g is the glass transition temperature of a copolymer composed of two monomer units A and B with mole fractions m_A and m_B, and T_{gA} and T_{gB} are, respectively, the T_g values of the homopolymers of A and B. The failure, in predicting T_g values, of linear relations including the reciprocal expression like the Fox equation[2] represents

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the significance, to molecular motions, of the arrangement of monomers in the polymer chain as well as the chemical composition.

Effects of the monomer arrangement or sequence distribution on T_g have successfully been considered, independently, by Barton[3] and by Johnston:[4] an extra term for diad sequences AB and BA was added, respectively, to the DiMarzio–Gibbs equation and to the Fox equation. The population of sequences AB and BA were estimated from the knowledge of copolymerization kinetics. Although apparent uses of those equations are different, i.e., linear plots[3] and computer fitting,[4] those equations are in a way the same for taking the effects of diad sequences AB and BA into account.

Admittedly, the contributions of Barton and of Johnston are landmarks in the progress of copolymer glass transition study.[1,5–13] Yet, the intrinsic characteristics of their equations have not been examined so far analytically.

This paper derives two new expressions of the Barton equation and describes remarkable characteristics of the equation. Those allow us to estimate, with minimum data, the whole behavior of copolymer glass transition with varying degrees of sequence distribution. Applications of the new expressions to some of the literature data are illustrated as demonstrations of potentials of the equations.

Diad Model for Copolymer T_g

In a copolymer formed from two monomer units A and B, there are four possible diad sequences: AA, BB, AB, and BA. Since the stiffness of an AB linkage is, in general, not equal to that of an AA or a BB linkage, eq 1 should be modified, as first suggested by Ellerstein,[10] as follows:

$$T_g = m_{AA}T_{gAA} + m_{BB}T_{gBB} + (m_{AB} + m_{BA})T_{gAB} \quad (2)$$

Here, T_g is the glass transition temperature of a copolymer *with composition and sequence distribution* specified by the values of m_{IJ}. T_{gAA} and T_{gBB} are, respectively, the T_g values of the homopolymers of A and B, and T_{gAB} is the T_g of the corresponding strictly alternating copolymer. Equations similar to eq 2 have been proposed by Barton,[3] by Uematsu and Honda,[11] and by Hirooka and Kato,[13] but they differ only in the definition of their parameters m_{IJ}. In this paper, a simple case is considered: the number of possible rotatable units in a copolymer chain is assumed to be the same as that of the monomers themselves. So we are concerned with the glass transition of addition polymers, not with condensation polymers having rigid units as part of the skeletal structure.

The parameter m_{IJ} in this paper is, like that of Barton, the mole fraction of the diad sequence IJ. This is given by the I mole fraction multiplied by the probability P_{IJ} that a given I monomer has a J monomer on its right: $m_{AA} = m_AP_{AA}$, $m_{BB} = m_BP_{BB}$, $m_{AB} = m_AP_{AB}$, and $m_{BA} = m_BP_{BA}$. The probability P_{IJ} has been calculated by Alfrey and Goldfinger[14] and lately by Harwood and Ritchey.[15] The latter introduced a new index, termed the run number, quite useful for characterizing sequence distribution.

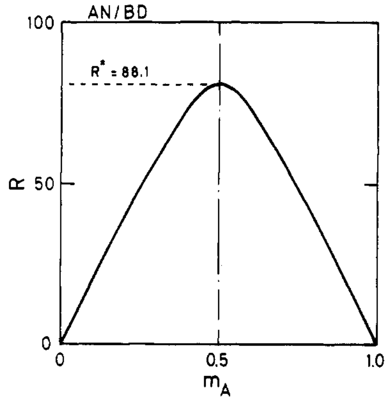

Figure 1. Variation of the run number R with composition for the system acrylonitrile/butadiene (AN/BD). The value of r_Ar_B, 0.054, as obtained from the R values reported,[16] was used.

The run number R is defined as the average number of both A and B monomer sequences (runs) occurring in a copolymer per 100 monomer units. If the number of sequences in a given copolymer is small like in block copolymers, that is obvious. If there are quite a few sequences, like in random copolymers, it is convenient to consider the copolymer to be cyclic, the number of sequences being counted, for example, counterclockwise. When the number of sequences is odd, this assumption dispenses with end effects, which will be of little significance for long-chain copolymers. The obtained number of sequences may be reduced to R, that per 100 monomer units. We may note that every run of A units is followed by a run of B units, and there are as many A runs as B runs in the copolymers. Those two types of runs are linked by an AB or BA diad, the number of these diads being equal to each other. Accordingly, the run number is equal to twice the percentage of AB or BA diads and also to the percentage of sum of these diads:

$$R = 100(2m_{AB}) = 100(m_{AB} + m_{BA}) \quad (3a)$$

Since a given A monomer has an alternative choice of A or B monomer on its right, the fraction of AA diads is equal to the A mole fraction minus the fraction of AB diads:

$$m_{AA} = m_A - m_{AB} = m_A - R/200 \quad (3b)$$

Similarly

$$m_{BB} = m_B - m_{BA} = m_B - R/200 \quad (3c)$$

Substitutions of these relations into eq 2 yield

$$T_g = m_AT_{gAA} + m_BT_{gBB} + (R/100)(T_{gAB} - \bar{T}_g) \quad (4)$$

with

$$\bar{T}_g \equiv (T_{gAA} + T_{gBB})/2 \quad (5)$$

without resorting to the expressions for P_{IJ}'s. This equation suggests plots of T_g against R in order to analyze the copolymer T_g dependence on sequence distribution. The data necessary for full description are the two T_g values of the homopolymers, the T_g of the alternating copolymer, and the R values for given random copolymers.

An estimate of R is possible directly from its composition and a nuclear magnetic resonance study[15,16] or indirectly by use of the relation

$$R = 400m_Am_B/[1 + (1 + 4m_Am_B(r_Ar_B - 1)^{1/2})] \quad (6)$$

Here, r_Ar_B is the product of the monomer reactivity ratios.[14,15] For later convenience, the variation of R with mole fraction in a copolymer is depicted in Figure 1. It can be noticed from this figure that R is symmetrical with respect to a line of $m_A = 0.5$ and R takes the maximum value R^* at the composition of $m_A = 0.5$.

Since the T_{gAB} is often unknown due to the difficulty in preparation of strictly alternating copolymers, we consider another expression including no T_{gAB} as a parameter. For a random copolymer with $m_A = m_B = 0.5$, eq 4 reads

$$T_g(m_A = 0.5) \equiv T_g(R^*) = \bar{T}_g + (R^*/100)(T_{gAB} - \bar{T}_g) \quad (7)$$

Elimination of T_{gAB} from eq 4 and 7 yields

$$T_g = m_AT_{gAA} + m_BT_{gBB} - (R/R^*)[T_g(R^*) - \bar{T}_g] \quad (8)$$

Since $T_g(R^*)$ is determined on equimolar random co-

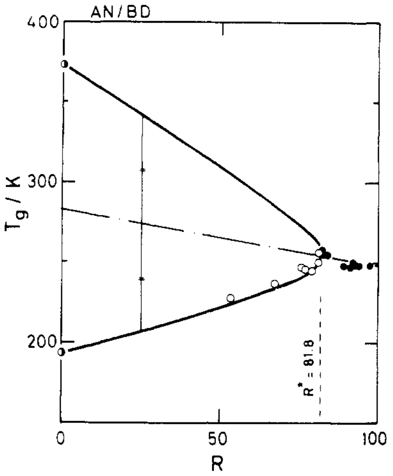

Figure 2. Plot of T_g against R for AN/BD (○) random and (●) alternating copolymers and (◑) the two homopolymers.[16] Solid line, the prediction of eq 4; dash-dot line, the locus of the middle point of T_g values predicted for random copolymers at a given value of R.

polymers preparable with ease, eq 8 could be more useful than eq 4. In practice, however, significant algebraic characteristics can be found from these equations. (i) When plotted against R, the three points $\bar{T}_g$, $T_g(R^*)$, and T_{gAB} are *on* the same straight line. (ii) T_g values for two random copolymers having a given value of R but different compositions deviate *by an equal distance* from the line mentioned above.

Characteristic i is obvious from eq 7, where the following proportion holds: $[\bar{T}_g - T_g(R^*)]/[\bar{T}_g - T_{gAB}] = R^*/100$. Characteristic ii can be seen as follows. On the given conditions, two T_g values may be specified as $T_g(m_A)$ and $T_g(m_A' = 1 - m_A)$ and the common R value as R'. The arithmetic mean of the two T_g values, as expressed by eq 4, proves to be

$$[T_g(m_A) + T_g(m_A' = 1 - m_A)]/2 = \bar{T}_g + (R'/100)(T_{gAB} - \bar{T}_g) \quad (9)$$

The right-hand side of the above equation is nothing but the T_g point, at $R = R'$, on the line connecting $\bar{T}_g$ and T_{gAB}. In other words, the straight line is a locus of the middle points of $T_g(m_A)$ and $T_g(m_A' = 1 - m_A)$, or this line represents the $\bar{T}_g$ values of hypothetical equimolar copolymers with varying degrees of sequence distribution.

Accordingly, it can be seen that when plotted against R T_g is a bivalued function in the R range from zero to R^*, a pair of T_g values at a fixed value of R being separated equally from the line connecting the arithmetic mean of T_g values of the homopolymers and the T_g of equimolar random copolymers. An extention of the line to $R = 100$ meets the T_g of the alternating copolymer composed of the corresponding constituents.

Application

Three sets of the literature T_g data of random and alternating copolymers are to be compared with the prediction of eq 4 or 8. Those data were selected to show three different cases: T_{gAB} is lower or higher than either T_g of the corresponding homopolymers or in between these values.

Acrylonitrile/Butadiene Copolymers

The T_g data of this system reported by Furukawa and Nishioka[16] are plotted, in Figure 2, against R, the values of which have been determined directly by these authors. Actually, they made the same plot as Figure 2, unfortunately in the limited range of R from 80 to 100. Naturally, the behavior of T_g was only partly understood. The prediction, as illustrated in the figure, is based on eq 4 with the experimental data: 373.2 K for T_{gAA} of polyacrylonitrile, 193.2 K for T_{gBB} of polybutadiene, and 248.2 K for T_{gAB} of the alternating copolymers.

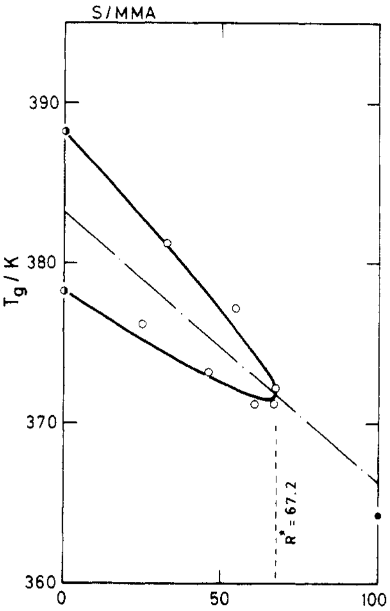

Figure 3. Plot of T_g against R for styrene/methyl methacrylate (S/MMA) copolymers:[12,13] for each symbol, refer to Figure 2. Solid line, the prediction of eq 8; dash-dot line, the line connecting $\bar{T}_g$ at $R = 0$ and $T_g(R^*)$ at $R = R^*$.

Now that Figure 2 is constructed, one can see the whole variation of T_g with sequence distribution. The prediction is in excellent accord with the data: the T_g data for random copolymers are close to the curve predicted, and the three points $\bar{T}_g(R = 0)$, $T_g(R = R^*)$, and $T_{gAB}(R = 100)$ seem to be on the straight line, as shown in the figure. The calculated value of $T_g(R^*)$, 254.8 K, agrees with the observed ones, 250.2 and 256.2 K, within experimental error of conventional T_g measurements. These agreements are invaluable because both T_g and R have been determined experimentally.

In addition, the prediction allows us to get good insights for T_g values of copolymers with sequence distributions not covered by experiment. It should be noted that the data points presented by solid circles in this figure are located in the usually inaccessible range of R from R^* to 100. This was accomplished by means of special control of the sequence regularity in copolymerization.

Styrene/Methyl Methacrylate Copolymers

The second set of T_g data to be analyzed is of the system styrene/methyl methacrylate. The data of Illers[12] and of Hirooka and Kato[13] are shown in Figure 3; where R values of random copolymer samples were calculated from eq 6 with the kinetic data reported,[13] $(r_A, r_B) = (0.52, 0.46)$. The prediction as shown by the solid line is based on eq 8 with the following data: 378.2 K for T_{gAA} of polystyrene, 388.2 K for T_{gBB} of poly(methyl methacrylate), and 371.7 K, on an average of two measurements, for $T_g(R^*)$.

Again, the agreement is satisfactory: the deviation of predicted T_g values from observed ones is less than 1 K. The T_{gAB} value as estimated by extending the line $\bar{T}_g - T_g(R^*)$ to $R = 100$ is 366.1 K, comparable with the observed value of 364.2 K. The minimum of T_g can be expected at the R value of 65.2, which corresponds to the styrene mole fraction of 0.57.

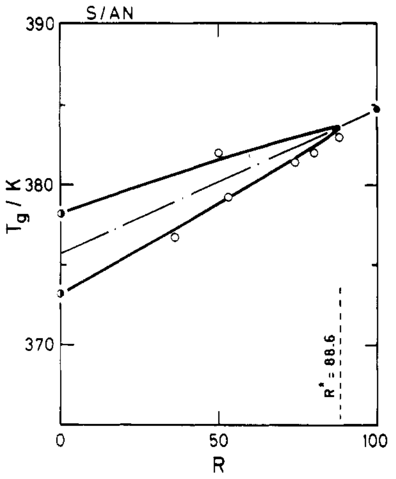

Figure 4. Plot of T_g against R for styrene/acrilonitrile (S/AN) copolymers:[4] for each symbol, refer to Figure 2. Solid line, the prediction of eq 4; dash-dot line, the line connecting $\bar{T}_g$ at R = 0 and T_{gAB} at R = 100.

Styrene/Acrylonitrile Copolymers

The third set is the data on styrene/acrylonitrile copolymers reported by Johnston.[4] Those T_g data are plotted in Figure 4 against R as calculated from eq 6 with his data,[4] (r_A, r_B) = (0.45, 0.02). The solid line is the prediction of eq 4 with 373.2 K for T_{gAA} of polystyrene, 378.2 K for T_{gBB} of polyacrylonitrile, and 384.7 K for T_{gAB} of the corresponding alternating copolymer. The prediction is seen to be in accord with the observed T_g values within 1 K. The expected $T_g(R^*)$ value of 383.9 K is compared with 383.0 K observed on a sample having the acrylonitrile mole fraction of 0.497.

Discussion

With the above three examples of analysis, the usefulness of eq 4 and 8 has successfully been demonstrated, although this success is essentially the reconfirmation of Barton's findings. Now we must examine the diad model, which the equations are based on.

The diad model has been called, in the study of copolymerization, the terminal model. Only the terminal unit of a growing polymer chain is postulated to affect the probability of monomer addition. So the monomer reactivity ratios, r_A and r_B, have been derived as parameters to characterize sequence distribution. Accordingly, a basic problem of copolymers is whether or not the systems we are interested in obey the theory based on the terminal model. The answer, we know, is that some do and some do not.

For the systems for which the terminal model holds, the sequence distribution can be estimated by using the values of r_A and r_B together with the composition. The populations of longer sequences like triads and pentads are also calculated in a similar fashion. On a line like this, Ham has extended the diad model of Barton for copolymer glass transitions to the triad model:[17] the T_g equation formally reads

$$T_g = m_{AAA}T_{gAAA} + m_{BBB}T_{gBBB} + m_{AAB}T_{gAAB} + m_{BAA}T_{gBAA} + m_{ABB}T_{gABB} + m_{BBA}T_{gBBA} + m_{ABA}T_{gABA} + m_{BAB}T_{gBAB} \quad (10)$$

Here, m_X and T_{gX} are, respectively, the mole fraction of and the T_g related to the sequence specified by the suffix X. Since there appear an untractable number of T_g values in the above equation, Ham reduced them to four: two homopolymer T_g values, T_{gAAB} (which is assumed equal to T_{gBAA}) and the fourth, coded as T_{gAB} (assuming the equality between T_{gABA}, T_{gBAB}, T_{gABB} and T_{gBBA}). Applying this extended equation to some published data on methyl methacrylate/acrylonitrile copolymers, he obtained improved agreement when certain values were assigned to T_{gAAB} and T_{gAB}.

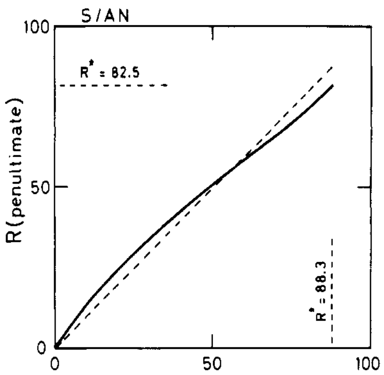

Figure 5. Comparison between the run numbers estimated with the terminal and penultimate models, based on the data of Hill et al.[20] for the system styrene/acrylonitrile.

However, the improvement obtained is difficult to understand. The equality between T_{gAAB} and T_{gABA} is merely an unverifiable assumption. In addition, the temperature difference of 14 K found between T_{gAAB} and T_{gABB} is not easy to conceive because the two homopolymer T_g values happen to be identical in this particular case.

Uematsu and Honda[11] tried also to reduce eight different triad sequences to three groups in four ways, effectively relating them to T_{gAA}, T_{gBB}, and T_{gAB}. In a certain way of reduction (case D in their Table I), they found the best agreement between theory and experiment. Yet, their way of reduction cannot be considered reasonable: triad BAB is related to T_{gAB}, ABA is not related to T_{gAB} but to T_{gBB}, BBA is related to T_{gBB}, AAB is not related to T_{gAA} but to T_{gAB}.

As has been clear from the illustrations of Barton[3] and of Johnston[4] as well as in the above section, the diad model is satisfactory in most cases. Any involved model, if necessary, should be investigated in the systems where the diad or terminal model fails.

An example of such a system is that of styrene and acrylonitrile, of which the T_g data have been presented in Figure 4. The point of discussion turns to be if the agreement can farther be improved with use of an involved model. In the study of copolymerization, the penultimate model has been developed for such systems. Since the triads are the basic units in this model, it is necessary to define four different monomer reactivity ratios, r_{AA}, r_{AB}, r_{BB}, and r_{BA}.[18] With use of those reactivity ratios and the molar compositions in feed, it is possible to calculate the run number.[15,19] Figure 5 shows such a result, in comparison with the run number estimated by the terminal model, for the system styrene/acrilonitrile with use of the data by Hill et al.:[20] as penultimate reactivity ratios, r_{AA} = 0.229, r_{AB} = 0.091, r_{BB} = 0.039, and r_{BA} = 0.634; as terminal reactivity ratios, r_A = 0.331 and r_B = 0.053 (slightly different from Johnston's data due probably to the difference in polymerization temperature). The deviation, negative or positive, from the broken line (as can be seen in Figure 5) must be taken into account for the R values of the data in Figure 4.

On the other hand, the T_g predicted for a random copolymer is formally written as eq 10 in the penultimate or triad model. The mole fractions of the triad sequences have been calculated by Ito and Yamashita,[19] with four monomer reactivity ratios and the compositions in feed. The eight different T_g values are again untractable, however. Without ambiguous assumptions to T_g values related to the respective triad sequences, it is impossible to draw the prediction in the figure. What is worse, such assumptions are not expected to be examined by experiments.

In conclusion, the diad model seems satisfactory to describe the dependence of copolymer T_g on composition and sequence distribution. Both equations of Barton and of Johnston are seen to work for the three systems shown in Figures 2–4 and also for the five others, with an exception, whose T_{gAB} values have been reported.[13] The exception is the system vinylidene chloride/methyl acrylate. For T_{gAB}, 357.5 K has been predicted by the Barton equation,[3] while the experimental value of Hirooka and Kato[13] was 325.7 K, some 22 K lower than the prediction. This significant disagreement and detailed comparison of the Barton equation with the Johnston equation remain for consideration in subsequent papers.

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Concentration-Dependent Collapse of Polymer Gels in Solution of Incompatible Polymers

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ABSTRACT: The volume change of polystyrene (PS) gels in a semidilute solution of poly(methyl methacrylate) (PMMA)/benzene was measured as a function of PMMA concentration for various PMMA molecular weights and degrees of cross-linking of the gel. In the case of small PMMA compared with the mesh size of the gel, a sharp transition from the swollen state to the collapsed state was observed with increasing PMMA concentration. The transition amplitude increased with decreasing PMMA dimension relative to the mesh size of the gel, and the transition concentration of PMMA increased with decreasing PMMA molecular weight, being independent of the degree of cross-linking. The deswelling behavior was analyzed on the basis of scaling concepts and described by a scaled form in a good approximation.

Introduction

Swelling and deswelling behavior of chemically cross-linked polymer gels is a rather old problem but has become of recent interest again because of newly developed aspects in this field: new approaches of rubber elasticity,[1] a phase transition with critical phenomena in swollen gels discovered by Tanaka,[2] and scaling arguments for semidilute solutions.[3] A swollen polymer gel immersed in the solution of a linear polymer shrinks as the concentration of the linear polymer increases because of reduction in effective solvent quality of the polymer solution.[4-8] Recently, Bastide et al.[9] investigated the volume change of polystyrene gels in toluene with incorporating linear polystyrenes in dilute and semidilute regions and interpreted the shrinking behavior of the gels on the basis of scaling concepts. This paper will deal with the gel deswelling by incorporation of incompatible linear polymers in the solvent. The deswelling behavior has some similarities to the collapse of single polymer chains by changing the solvent quality. In fact, Erman and Flory[10] have recently treated both problems on the same theoretical basis. Concentration-dependent collapse of single chains in the semidilute solution of incompatible polymer was studied theoretically by Tanaka[11] and Nose[12] and experimentally by Lerman,[13] Laemmli,[14] and Ushiki and Tanaka,[15] but no study on gel collapse has been reported to our knowledge.

For this problem, we can consider various cases according to the combination of the mesh size ξ_e of gels in the swollen state, the chain dimension R_g of the incorporated linear polymers, and compatibility of the linear polymers with the gel polymers which is characterized by the χ-parameter for segment interactions between them. (Hereafter, the solvent is considered to be thermodynamically good for the both polymers.) In case of $R_g > \xi_e$, the gel shrinks gradually when the concentration of the linear polymer ϕ_l increases, passing through the overlap concentration ϕ^*, and eventually it changes its volume such that $\phi_g \simeq \phi_l$, where ϕ_g is the volume fraction of polymers in the swollen gel. In this case of $R_g > \xi_e$, the linear polymer cannot interpenetrate into the gel and the equi-

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